Computational Protocols for Viscosity Reduction in CO$_2$ Capture Organic Solvents

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Program goals and objectives

- Enable solvent design for advancement up DOE’s TRL scale to enable large-scale testing and deployment by year 2030

- Develop tools and solvent design methodologies for viscosity prediction/reduction across all transformational solvent platforms
  - Understand the underlying molecular descriptors that control viscosity
  - Develop viscosity reduced order model that can predict key solvent physical and thermodynamic properties
  - Given a library of compounds, down-select to a small number that can reduce viscosity of current formulations by >400 cP or more

- Apply the developed viscosity model and molecular design principles to other solvents in DOE’s post-combustion solvent portfolio

- Budget-permitting, conduct a bench-scale demonstration of the most advanced solvent that includes extended testing with and without water.
  - Use bench-scale testing data to make energy and LCOE predictions for a full-scale system, using Aspen Plus™ to model the system
The challenges of solvent development

The viscosity of the medium changes with CO$_2$ loading

Different R groups generate a big number of compounds to be screened

Neutral, non-viscous

Ionic liquid forms upon CO$_2$ capture (but does it have to?)
Example library of CO$_2$BOLs – Round 1

$\sim 10^2$-$10^3$ molecules that need to be screened quickly and reliably and scaled up

August 11, 2016
Initial molecular design metrics

What we need (specific for each solvent class):

- Guanidine-based CO₂BOLs
  - High basicity needed for >90% CO₂ capture
  - Zwitterionic form has low volatility
- Cyclic base core to prevent hydrolysis

Initial design concepts:

- Optimize cation-anion interactions in the Zwitterion
- Steric effects
- Fine tuned molecular electronics
- Effect of hetero-atoms

Steric Effects

Electronic Effects

Silane-Based CO₂BOLs

August 11, 2016
Scientific and technology approach

Model Validation and Refinement of Design

Molecular Library Design

Experimental Measurements

Molecular Modeling and Property Prediction

Synthesis and Characterization

Molecular structure and chemical formulas.
Molecular modeling tools

- **DFT-based electronic structure for molecular properties** (~$10^2$-$10^3$ atoms)
  - Accurate description of molecular properties
  - Atomic charges needed for classical potential
  - Reaction energetics: H-bonding, CO$_2$ absorption energy

- **Ab initio Molecular Dynamics and accelerated free energy sampling methods** (metadynamics, Blue moon, ~$10^3$ atoms)
  - Reactivity including temperature effects and dynamic behavior, free energy estimates

- **Classical Molecular Dynamics (MD)** (~$10^4$-$10^5$ atoms)
  - Accurate description of molecular liquid structure, with potentials derived from electronic structure (Universal OPLS with ab initio charges)
  - Obtain number and type of relevant intermolecular contacts
  - Transport properties: diffusion and viscosity

- **Codes, Software:**
  - CP2K (www.cp2k.org), NWChem (www.nwchem.org), Gaussian09 (http://www.gaussian.com/g_prod/q09.htm)
  - Viscosity can be directly computed from long simulations (1µs), Software: GROMACS (www.gromacs.org)

- **Desired outcome is a reduced model**
  - Shift through many candidates in short time (few days)
CO$_2$BOLs – Initial computation targets

- Initial and new computational targets
  - 3-D steric interactions
  - Reduced intermolecular interactions
- Simulate pure liquids and mixtures at 15%, 25%, and 50%, determine viscosity from analysis of trajectories
- Evaluate inter- vs intra-molecular hydrogen bonding effects on viscosity

**Control Molecules & Complexes**

- Initial best-performing BOL
  - Viscosity ~ 200cP at 0.25 mol %CO$_2$
- Poor performing BOL
  - Viscosity >>1,000 cP at 0.25 mol %CO$_2$

**Initial trial Molecules & Complexes**

- Preserves weights and functional groups of Current BOL (2$^{nd}$ amine and alcohol, i.e. similar CO$_2$ adsorption energy)
- Partially restrict mobility of aliphatic side chain w. 2$^{nd}$ ring.
- May favor internal H-Bond.
- May be a more readily synthesizable target.
- Preserves weights and functional groups of Current BOL (2$^{nd}$ amine and alcohol, i.e. similar CO$_2$ adsorption energy)
- Restrict mobility of aliphatic side chain w. 2nd ring.
- Hinders internal H-Bond.

August 11, 2016
Validation of molecular model

<table>
<thead>
<tr>
<th>System</th>
<th>Experimental values (cP)</th>
<th>Calculated viscosities from MD (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure (0% CO₂)</td>
<td>8</td>
<td>15</td>
</tr>
<tr>
<td>15% mol CO₂ loading</td>
<td>36</td>
<td>35</td>
</tr>
<tr>
<td>25% mol CO₂ loading</td>
<td>110</td>
<td>150</td>
</tr>
<tr>
<td>50% mol CO₂ loading</td>
<td>~3000²</td>
<td>&gt;1000</td>
</tr>
</tbody>
</table>

1DJH et al. 2014, Energy Procedia 63, 8144-8152, in press. ²ASPEN Plus projection
Molecular level interactions: Hydrogen bond

Low viscosity

Internal H-bond, 34% of zwitterionic species

~1.65 Å

Extended liquid structure

External H-bond

Internal H-bond

High viscosity

Advanced molecular design:
Locking in the internal H-bond (~80%)
Lower projected cP at all CO₂ loadings
At 50%:
  KOL >1500 cP
  VOL ~800 cP

Molecular level interactions:
Hydrogen bond
Low viscosity

Internal H-bond, 80% of zwitterionic species

1.65 Å

Internal H-bond

Advanced molecular design:
Locking in the internal H-bond (~80%)
Lower projected cP at all CO₂ loadings
At 50%:
  KOL >1500 cP
  VOL ~800 cP
Molecular modifications that have deliberate effect on viscosity

- Ether groups close to the CO₂ binding site increase the % of zwitterionic molecules with internal hydrogen bonds in Koechanol.
- MD predicts a 30% reduction in the viscosity of ether Koechanol compared to Koechanol, both at 25% mol CO₂ loading.
  - Koechanol (34% internal H-bond and 10% stacking) 150 cP
  - Ether open Vandanol
    - (61% internal H-bond)
    - (20% stacking)
    - 120 cP

Ether Koechanol
(52% internal H-bond)
(9% stacking)
100 cP (MD)
exp. observation, lower than Koechanol
Towards a reduced model: thermodynamics of CO$_2$ binding

- CO$_2$ binding free energy, optimally ca -15 to -20 kJ/mol
- Red line is binding free energy from blue moon dynamics, blue line is $\Delta E$ from AIMD
- Confirmation of the equilibrium from NMR data

Viscosity dependency on loading

- Exponential dependency on loading.
  - Dependence confirmed by MD and experiment
Reduced Model: Explicit H-Bonding

\[ \eta = c_1 \ln \left( \frac{P_{int}}{1 - P_{int}} \right) \exp (c_2 L) \]

- If \( r_{O-H} > 2.0 \text{ Å} \), then \( P_{int} = 0.001 \)
- If \( r_{O-H} < 2.0 \text{ Å} \), then
- Difference between electrostatic repulsion (NO) and attraction (OH)

\[ X = \frac{q_N q_O}{r_{NO}} + \frac{q_O q_H}{r_{OH}} + \frac{q_N q_H}{r_{NH}} \]

\( P_{int} = aX + b \)

From MD or DFT

From DFT (ESP charges)

Viscosities (cP) from classical MD

\[ R^2 = 0.96 \]

D. C. Cantu et al. submitted
Structure/Viscosity Correlations

- The reduced model recovers ~80% of the H-bonding determined by MD
- Over 90% of correlation between viscosity and H-bonding by either MD (A), or RM (B)
First cycle: 200 compounds screened by molecular simulation and reduced models
- Predicted viscosities
- CO$_2$ binding energy

Approximately 25 compounds by full MD of liquid state

Down-selected to 5 best candidates for further investigation
- Full MD to validate/tune reduced model
- Synthetic targets
Another 100 compounds screened in cycle-2

![Chemical structures](image)

275  94,139  228  170  111  146

36  13  n/a, 14  33  29  n/a

14  n/a  14  145  198

*IPADM-2-BOL = 150 cP*
Best five candidates not exp. verified yet.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Pint Model Predicted</th>
<th>ΔΔE (kJ/mol) (CO₂ BE)</th>
<th>η (cP) (25%) Reduced</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>92%</td>
<td>-1.2</td>
<td>12</td>
</tr>
<tr>
<td>2</td>
<td>90%</td>
<td>-2.0</td>
<td>15</td>
</tr>
<tr>
<td>3</td>
<td>85%</td>
<td>-5.3</td>
<td>23</td>
</tr>
<tr>
<td>4</td>
<td>83%</td>
<td>-7.3</td>
<td>27</td>
</tr>
<tr>
<td>5</td>
<td>76%</td>
<td>-9.1</td>
<td>40</td>
</tr>
</tbody>
</table>

Viscosity of original IPADM-2-BOL at 25% ~150 cP
ΔΔE computed relative to IPADM-2-BOL
Novel insight from MD: Neutral capture

Dynamic equilibrium between Zwitterion and its acid equivalent

Theoretical suggestion: Non-ionic CO$_2$ capture solvent systems

We determined the acid-base equilibrium of several model CO$_2$BOL systems.

- We found that we can modify the electronic structure of the molecule to shift the equilibrium towards a neutral CO$_2$ binding species.
- Preliminary data of viscosities from classical MD simulations indicate significant improvement.

<table>
<thead>
<tr>
<th>25% mol CO$_2$ loading</th>
<th>IPATFMM-2-BOL Viscosity (cP)</th>
<th>EODM-2-BOL Viscosity (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>All zwitterion</td>
<td>328.5</td>
<td>45.5</td>
</tr>
<tr>
<td></td>
<td>+415.4 - 117.7</td>
<td>+8.0 - 5.9</td>
</tr>
<tr>
<td>1:1 acid:zwitterion</td>
<td>214.2</td>
<td>17.9</td>
</tr>
<tr>
<td></td>
<td>+45.0 - 31.7</td>
<td>+1.9 - 1.6</td>
</tr>
<tr>
<td>All acid</td>
<td>137.9</td>
<td>14.2</td>
</tr>
<tr>
<td></td>
<td>+21.3 - 16.3</td>
<td>+0.7 - 0.6</td>
</tr>
</tbody>
</table>

Neutral capture is more impactful at higher loadings

A

IPADM-2-BOL

B

% mol CO₂ loading

0%  10%  20%  30%
The same principles apply to different solvents: Class 2 GE solvents

- Model validation
- GAP class of solvents
- CO₂ loadings (mol %): 0, 25, 50
- Densities at 40, 80 and 120 °C
- Heterogeneous solvent: different phases

<table>
<thead>
<tr>
<th>System</th>
<th>Density at 40 °C</th>
<th>Density at 80 °C</th>
<th>Density at 120 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>GAP-0/TEG 0% CO₂</td>
<td>975.5 kg/m³</td>
<td>932.7 kg/m³</td>
<td>884.6 kg/m³</td>
</tr>
<tr>
<td></td>
<td>exp: 844.2 (5% error)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GAP-0/TEG 25% CO₂</td>
<td>992.5 kg/m³</td>
<td>952.3 kg/m³</td>
<td>906.6 kg/m³</td>
</tr>
<tr>
<td>GAP-0/TEG 50% CO₂</td>
<td>1008.7 kg/m³</td>
<td>970.6 kg/m³</td>
<td>927.4 kg/m³</td>
</tr>
<tr>
<td>GAP-1/TEG 0% CO₂</td>
<td>969.0 kg/m³</td>
<td>917.9 kg/m³</td>
<td>869.5 kg/m³</td>
</tr>
<tr>
<td></td>
<td>exp: 1000.1 (4% error)</td>
<td>exp: 982.7 (7% error)</td>
<td>exp: 859.8 (1% error)</td>
</tr>
<tr>
<td>GAP-1/TEG 25% CO₂</td>
<td>983.7 kg/m³</td>
<td>939.2 kg/m³</td>
<td>892.7 kg/m³</td>
</tr>
<tr>
<td>GAP-1/TEG 50% CO₂</td>
<td>1003.6 kg/m³</td>
<td>960.8 kg/m³</td>
<td>915.8 kg/m³</td>
</tr>
</tbody>
</table>
GAP solvent structure

- CO₂ loadings (mol %): 0, 25, 50
- Preliminary viscosities at 40 °C
- Also starting temperature dependence runs

<table>
<thead>
<tr>
<th>System at 40 C</th>
<th>0% mol CO₂</th>
<th>25% mol CO₂</th>
<th>50% mol CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>GAP-0/TEG</td>
<td>26 ±5/-4 cP</td>
<td>65 ±14/-10 cP</td>
<td>154 ±35/-24 cP</td>
</tr>
<tr>
<td>GAP-1/TEG</td>
<td>9 ±1/-1 cP (exp: ~19 cP)</td>
<td>51 ±23/-11 cP (exp: ~ 90 cP)</td>
<td>*</td>
</tr>
</tbody>
</table>

*: in progress

- Heterogeneous solvent structure

CO₂-GAP-0: red
GAP0: blue
TEG: silver
As in Ionic Liquids, H-bonds between RNH$_2^+$---OOCN are present in the extended liquid structure.

- GAP-0 in TEG (40% wt)
- CO$_2$ loadings (mol %): 0, 25, 50
- Because CO$_2$-loaded molecules cluster, they form strong H bonds (RNH$_2^+$ to NCOO$^-$) within the molecule, and with other molecules.

“Closed” conformation
H-bond within molecule

“Open” conformation
No H-bond within molecule

H-bonds present between one “closed” CO$_2$-GAP-0 and one “open” CO$_2$-GAP-0
Screen 50 compounds for acid/base equilibrium

- Screen 50 compounds for CO₂-binding energy and acid/base equilibrium
- Known and new compounds
- Acid/base properties of 14 compounds still running or being double checked
  - Preliminary data presented here

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>Acid/Base Eq ΔE(A-Z) in kJ/mol Keq=[A]/[Z] at 40 °C</th>
<th>CO₂ Binding Within 25 kJ/mol of the CO₂ binding energy of GAP-0 or GAP-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>GAP-Dytek</td>
<td><img src="image1" alt="Structure" /></td>
<td>-4.6 (\sim 5/1)</td>
<td>Yes</td>
</tr>
<tr>
<td>GAP-Et</td>
<td><img src="image2" alt="Structure" /></td>
<td>+41.5 all zwitterionic</td>
<td>Yes</td>
</tr>
<tr>
<td>GAP-Ib</td>
<td><img src="image3" alt="Structure" /></td>
<td>-8.2 (\sim 23/1)</td>
<td>Yes</td>
</tr>
</tbody>
</table>
Design principles for neutral capture apply in new solvent class (PNNL, patent pending)

Equilibrium strongly shifted towards the neutral
Three different classes of compounds, a common behavior

Class 1: PNNL CO2BOLS
Class 3: GE GAP Class
Class 3: PNNL New, all Z
Class 3: PNNL New, Z:A =1:1
Class 3: PNNL New, all A
Class 3: PNNL new system

Radial Distribution

Class 3: PNNL New, all Z
Class 3: PNNL New, all A
Class 3: PNNL New, all A
Class 3: PNNL new system

Radial Distribution

Radial Distance (Å)

Class 3: PNNL New, all Z

Zwitterion-Zwitterion
Zwitterion - Alcohol

Acid - Acid
Acid - Alcohol

Class 3: PNNL New, all A
Molecular simulations were used to identify the critical structure property factors that affect viscosity in three different classes of CO$_2$ capture solvents:

- Class 1, PNNL CO2BOLs
- Class 2, GE GAP solvents
- Class 3 PNNL new single component solvents

A reduced order model was constructed that can be used for quick and reliable screening
- Can be adjusted to fit other classes

Novel insights pointing at neutral capture have the potential of drastic viscosity reductions in all classes of solvents
THANK YOU FOR YOUR ATTENTION!